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Self-assembled nanocomposite organic–inorganic proton conducting sulfonated poly-ether-ether-ketone (SPEEK)-based membranes: Optimized mechanical, thermal and electrical properties

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ABSTRACT

Mechanical, thermal and electrical properties of polymer blends of SPEEK with 7% SiPPSU are reported. Presence of silicon stabilizes the polymer morphology. The glass transition temperature, determined by dynamic mechanical analysis, depends more on blend formation than on degree of sulfonation. The water uptake coefficients, determined in liquid water and water vapour, are strongly reduced by the presence of the secondary silylated phase, so that blend membranes do not dissolve in water even at 140 °C. The electrical conductivity is of the order of pure SPEEK and does not degrade even at high relative humidity. The sum of these properties make these self-assembled nanocomposite membranes most attractive for use in intermediate temperature PEMFC.

1. Introduction

The future of polymer electrolyte membrane fuel cell (PEMFC) technology depends critically on the resolution of a number of material problems, especially development of more appropriate and less expensive electrodes and inexpensive high performance PEMs [1–3].

We have developed in recent years several new proton-conducting membranes, based on modification of aromatic polymers [4–6]. The studied polymers belong to the poly-ether-ether-ketone (PEEK) and poly-phenyl-sulfone (PPSU) families [7,8]. These fully aromatic polymers have attractive properties: they are inexpensive and widely available; they are thermally and chemically stable against oxidation and reduction; and they can be functionalized [9,10]. The base polymers are sulfonated by different sulfonating agents [11–13]. Sulfonated PEEK (SPEEK) membranes present hydrophobic domains, containing the aromatic backbone, and hydrophilic domains, where dissociated sulfonate groups, hydronium ions and water molecules are present [14,15]. On one hand, the presence of hydrophilic domains permits proton conduction and a certain amount of water is necessary for a sufficient proton conductivity of the membranes. On the other hand, an excess of water leads to morphological instability and the membrane swells at too high relative humidity, leading to degradation of conductivity [16–18]. It is therefore quite clear that water balance during fuel cell operation is a very sensitive parameter for correct functioning. There exists an optimal window for each material, which depends also on the temperature range. In fact, operation at temperatures above 100 °C is a main objective of fuel cell development for well established reasons: (i) faster electrochemical kinetics enables reducing the fuel cell stack with identical power, (ii) faster desorption kinetics of CO on platinum reduces the need for fuel purification and CO concentrations above 10 ppm in hydrogen become acceptable, and (iii) smaller radiator area is possible in fuel cell cars. A temperature range around 120–130 °C is therefore worthwhile and a relative humidity below 35% is recommended, given that water vapour pressure above 1 atm would require expensive pressurization devices [19,20].

To improve water retention and morphological stability of sulfonated aromatic polymers, different strategies have been explored. We have prepared nanohybrid organic–inorganic materials containing silicon as inorganic component following a bottom-up approach. Silicon was covalently linked to the polymeric backbone in order to enhance homogeneity, mechanical strength and morphology [21].

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An alternative top-down approach is to mix preformed components in order to obtain a nanocomposite object [22,23]. Different types of nanocomposites can be discussed, depending on the bond type between the two phases [24,25]. The basic concept is to intimately mix a highly proton conducting polymer, which may suffer from morphological instability due to a large concentration of sulfonic acid groups, with a minority, “anchor” phase, whose main property is to maintain the morphology of the composite. To do so, the secondary phase should therefore have a high mechanical strength.

We have previously reported different secondary phases, based on sulfonated and silylated PPSU. PPSU was chosen because it combines affinity with SPEEK with strong intermolecular interactions, solubility in organic solvents, allowing easy functionalization; polymers containing a covalently linked silicon moiety were observed to have good mechanical and water uptake properties. The best results were obtained for composites with 7 wt% only silylated PPSU [8,26].

In this work, we report the relevant parameters of this new membrane type, including mechanical and thermal properties, water uptake, and proton conductivity.

2. Experimental

2.1. Membrane synthesis

Sulfonated PEEK was prepared by reaction of PEEK (Victrex 450P, MW = 38300) with concentrated sulfuric acid at 50 °C for 20 or 120 h to obtain two different degrees of sulfonation (DS) [11]. The solution was poured under continuous stirring into a large excess of ice-cold water. After standing overnight, the white precipitate was filtered and washed several times with cold water to neutral pH. The sulfonated polymer (SPEEK) was then dried for 17 h at 80–85 °C. The degree of sulfonation was evaluated both by ^{1}H NMR [27] and by titration: DS was 0.75 or 0.9.

Silylated PPSU (SiPPSU) can be synthesized by metalation reaction of PPSU with butyl-lithium (BuLi), followed by electrophilic substitution by phenyl-trichlorosilane ($PhSiCl_3$). The original polymer PPSU (Solvay, MW = 46173) was added in nitrogen atmosphere to anhydrous tetrahydrofurane. The solution was stirred at room temperature for 1 h then cooled to −60 °C. After 1.5 h, an excess of BuLi and tetramethylenediamine (TMEDA) were added and the solution was stirred for 2 h at −60 °C. At this point, $PhSiCl_3$ (Aldrich, 97%) was added and the solution was slowly warmed to room temperature and then kept at reflux for 2 h. The precipitate formed, SiPPSU, was filtered and washed with water until no chlorides were detected. The characterization of SiPPSU was already reported [8].

The procedure for membrane preparation was solution casting using dimethylsulfoxide (DMSO). In a typical experiment, around 250 mg sample were prepared by dissolving 93 wt% SPEEK with DS = 0.75 or 0.9 in 30 mL of solvent and 7 wt% SiPPSU was added and sonicated for 48 h. The resulting suspension was stirred for 4 h, evaporated to 5 mL, cast onto a Petri dish and heated to dryness. After cooling to room temperature, the resulting membranes were peeled off and treated under dynamic vacuum 24 h at 80 °C for solvent removal. Subsequent thermal treatments of membranes were performed at 140 °C for 64 h.

2.2. Thermoanalytical characterization

The thermal degradation of polymer membranes was investigated by High Resolution Thermogravimetric Analysis (TGA Q500, TA Instruments), performed between 25 and 600 °C with a maximum heating rate of 5 K min^{-1} under air flux in platinum sample holders.

Dynamic Mechanical Analysis (DMA) was performed on a DMA 2980 apparatus from TA Instruments in tension mode with samples of approximately 15 mm × 7 mm size and 90 μm thickness. DMA was operated in air at a fixed frequency of 1 Hz with a 1N applied pre-force and oscillation amplitude of 10 μm. This last value was chosen to keep the linear viscoelastic domain of samples during experiments. The storage (E') and loss modulus (E'') spectra versus temperature were obtained at 3 K min^{-1} between 50 and 250 °C.

Dielectric analysis (DEA) measurements were performed using a DEA 2970 dielectric analyzer from TA Instruments with ceramic parallel plate (CPP) configuration of electrodes. This apparatus allows a frequency scan ranging from 10 Hz to 100 kHz. All experiments were performed on 25 mm × 25 mm membrane samples under dry argon atmosphere at a gas flow rate of 500 ml min^{-1} and with heating rate of 2 K min^{-1}. The measured current was separated into its capacitive and conductive components. An equivalent capacitance and conductance were then calculated and used to determine the dielectric permittivity ε' and the dielectric loss factor ε'', which is proportional to conductance. Ionic conductivity was calculated as follows:

$$\sigma = \varepsilon_0 \varepsilon'' \omega \qquad (1)$$

where ε_0 is the absolute permittivity of the free space ($\varepsilon_0 = 8.85 \times 10^{-12}\ F\,m^{-1}$) and ω is the angular frequency of the applied sinusoidal voltage.

2.3. Proton conductivity measurements

Through-plane conductivity measurements were carried out on membranes, 8 mm in diameter and 90 μm thick, sandwiched between gas diffusion electrodes (ELAT containing 1 mg cm^{-2} Pt loading), which were pressed on the membrane faces by means of

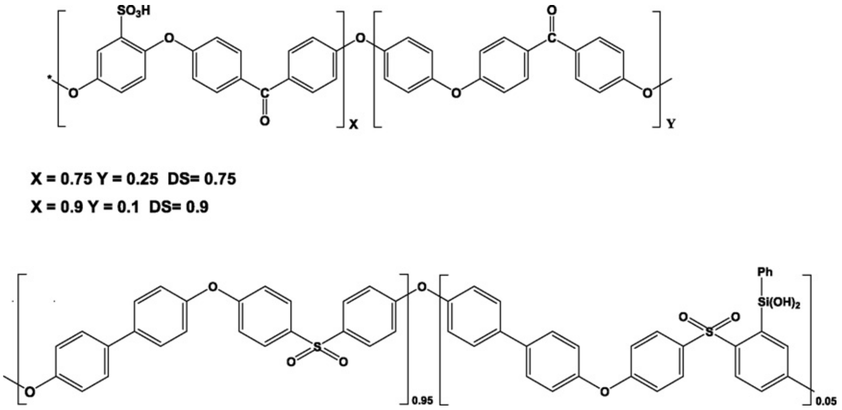

Fig. 1. Formula of the blend components.

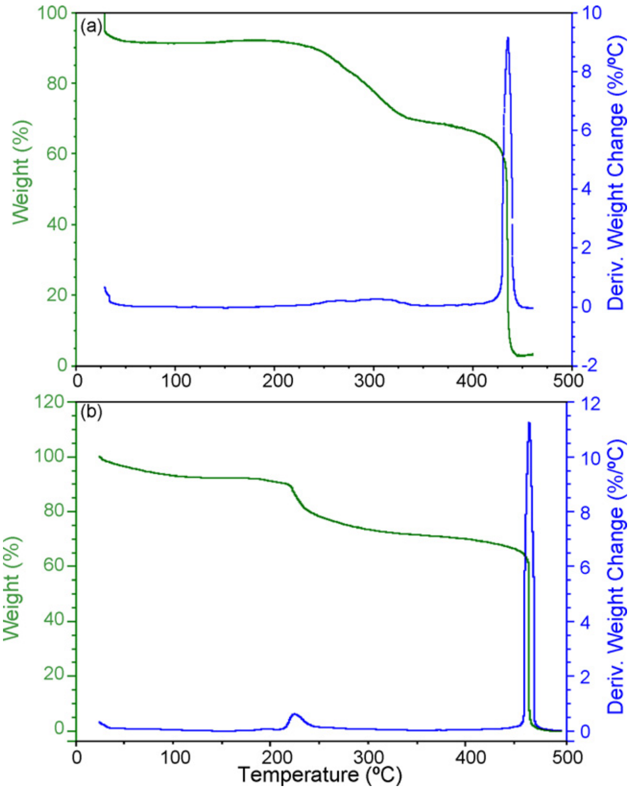

Fig. 2. High resolution thermogravimetric curve of (a) SPEEK 0.9–7% SiPPSU blend and (b) SPEEK 0.9.

porous stainless steel discs. The pressure clamping the membrane between the electrodes (60 kg cm^{-2}) was applied before starting the measurements and not controlled during the experiment. The membrane conductivity was determined as a function of temperature and relative humidity by impedance spectroscopy with a Solartron Sl 1260 Impedance/Gain Phase Analyser connected to a Solartron 1480 Multistat potentiostat–galvanostat in the frequency range 10 Hz to 1 MHz at a signal amplitude $\leq$100 mV. All reported conductivity values had reached a constant value for at least 2 h. Relative humidity in the range 80–150 °C was controlled as described in Ref. [16].

2.4. Water uptake measurements

Water uptake was measured by two complementary experiments. (i) By full immersion in deionized water at temperatures between 25 and 145 °C: polymer samples were weighed before and after immersion times between 1 h and 6 days (hydrothermal treatments above 100 °C were performed in hermetically closed Teflon vessels). After the immersion and before weighing, the membranes were equilibrated in deionized water at room temperature for 24 h [28]. (ii) By equilibration with water vapour at 25 °C under 0–95% RH. The water sorption isotherms were recorded using a TA5000 thermogravimetric analyzer. RH was modified in 5 or 10% steps and the water uptake recorded at each step during 2 h. Prior to all experiments, the membranes were first dried *in situ* 3 h at 80 °C under 0% RH.

3. Results and discussion

Fig. 1 shows the formula of the blend components. The polyarylether ketones or sulfones are a class of polymers consisting of sequences of 1,4-disubstituted phenyl rings separated by ether and carbonyl or sulfonyl linkages. PEEK and PPSU were chosen for their complementary chemical and morphological properties. Being fully aromatic, these polymers have excellent thermal oxidation resistance with a high glass transition temperature (T_g). The value of T_g depends on macromolecular characteristics affecting chain stiffness. Chain flexibility is diminished and glass transition temperature increased by presence of bulky side groups, polar side groups, aromatic chain groups, which tend to stiffen the molecular backbone.

An important aspect regards their conformational characteristics: the polymeric backbone of PEEK is more flexible while the molecular chain of PPSU is rather rigid. Both the direct linkage between the aromatic rings and the resonance effects due to the sulfonyl group contribute to its reduced flexibility. A more rigid polymer in which chain segments are unmoving in fixed positions has stronger intermolecular interactions. This behaviour is reflected in the Tg of the two polymers: 208 and 143 °C for PPSU and PEEK, respectively. Thus, the relatively linear conformation of SiPPSU, as previously reported [8], can be correlated to the rigidity of the polymer and to the bulky phenyl side group bonded to silicon that is stiff and near to the backbone and can cause steric hindrance, decreasing chain mobility. Depending on the molecular struc-

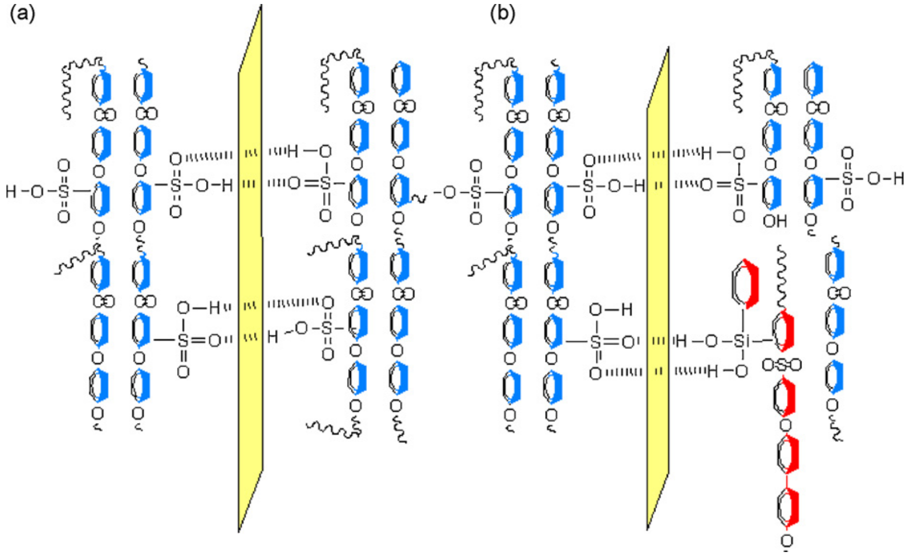

Fig. 3. Schematic representation of the interface between (a) SPEEK polymer chains and (b) SPEEK and SiPPSU chains.

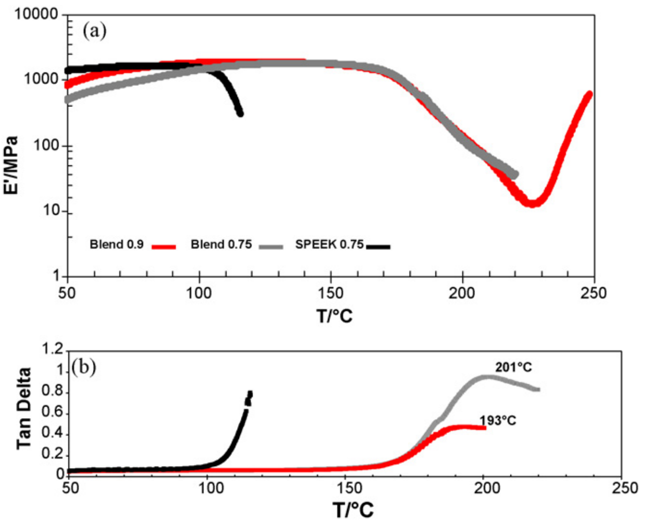

Fig. 4. Dynamic mechanical analysis curves of SPEEK/SiPPSU 7% blends with different degree of sulfonation, DS = 0.75 (grey symbols) or 0.9 (red symbols) and comparison with SPEEK at DS = 0.9 (black symbols). All samples are cured at 140 °C. (a) Storage modulus and (b) Tan delta.

ture and on the flexibility and conformation of macromolecules, different intermolecular bonding forces act among polymeric systems. In the arylen-based systems, different types of interactions between the polymer chains are always present: London-type interactions between the backbones, dipole–dipole interactions between the carbonyl or sulfonyl groups, hydrogen bridges and electrostatic interactions connected with the acidic groups present when the polymers are sulfonated [29]. The nature and quantity of these interactions determine the molecular aggregation of the system leading to different tertiary structures. The type of self-assembly plays a fundamental role in the polymer properties and determines the membrane behaviour [28]. Consequently the introduction of the second phase in SPEEK can lead to the formation of specific interactions between the polymer chains modifying the hydrophilic/hydrophobic domains and reinforcing the mechanical strength.

3.1. Thermo-mechanical properties and water uptake

Fig. 2 shows typical high resolution thermogravimetric curves of a blend and comparison with SPEEK (DS = 0.9). The initial mass loss (about 10%) corresponds to removal of water molecules from the polymer membrane. For the blend, one can estimate that about 2.5 water molecules are eliminated per sulfonic group (expressed as water uptake coefficient $\lambda = N_{H_2O}/N_{SO^{3-}}$) using the molar masses of water and polymer blend. One can then recognize the loss of sulfonic acid groups between 225 and 325 °C followed by the oxidative degradation of the polymer main chain around 430 °C [30]. In comparison with pure SPEEK, one notices an increase of the decomposition temperature of sulfonate groups, whereas the temperature of degradation is slightly lower, but completely sufficient for use in intermediate temperature fuel cells.

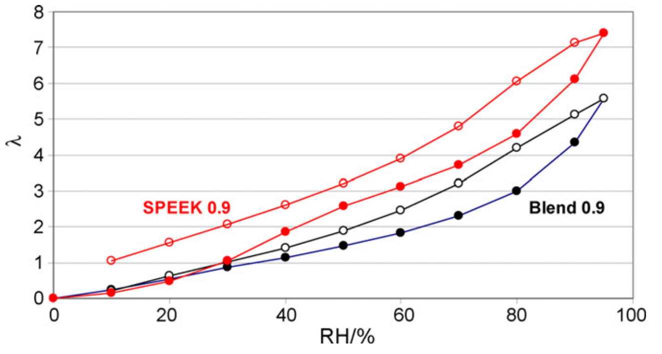

Fig. 5. Water adsorption/desorption isotherm for SPEEK 0.9 and SPEEK 0.9/SiPPSU blend at 25 °C.

The larger temperature range for loss of sulfonate groups, in comparison with pure SPEEK, indicates that interactions at the interface between the two polymers modify the intermolecular bond energetics, as schematically represented in Fig. 3, and lead to a larger distribution of decomposition temperatures. The interface represents also a region, where water molecules are preferably located, leading at high water partial pressure to the formation of hydrophilic conduction pathways. The symmetry break between the two polymer chains in the blend is clearly seen (Fig. 3b). The introduction of SiPPSU chains increases the hydrophobicity of the polymer blend and induces specific interactions in the system modifying the hydrophilic/hydrophobic domains. This model justifies the significant changes of water uptake and mechanical properties observed in the blends.

To study the effects of the molecular structure on polymer properties we performed a dynamic mechanical analysis. In fact, the mechanical behaviour of the membrane strongly depends on its preparation method, for instance thermal history and solvent casting [28,31]. Some residual DMSO, a very high boiling solvent, acting as a plasticizer, can also play an important role influencing the performance of the membranes.

Typical DMA curves in dry conditions presenting the real part of the complex modulus (storage modulus) *vs.* temperature of SPEEK (DS = 0.9) and blends with differently sulfonated PEEK are shown in Fig. 4a. The storage modulus varies strongly with temperature while there is no important influence of DS. The slight increase of strength with increasing DS can be related to the larger number of ionic interactions between the sulfonic groups in the macromolecular chains. The important storage modulus decrease observed above 170 °C for blends is related to the glass transition (Table 1), where a polymer softening is observed. As discussed above, limited chain mobility leads to a strong increase of T_g with respect to pure SPEEK [12,32]. A similar effect is expected due to the enhanced asymmetry of the system. The polymer softening is accompanied by a variation of loss modulus which results in a tan delta peak (Fig. 4b). This peak can also be used to determine the glass transition temperature of the polymer (Table 1). One can notice that if no influence of DS can be seen on storage modulus curves, Tg measured from tan delta peak is slightly decreasing with increasing DS [32]. Larger differences have been previously reported in literature for pure

Table 1
Water uptake coefficients λ and glass transition temperatures of blends.

Sample	Λ				T_g (°C)	
	Water temperature (°C)				Tan delta peak	E' onset
	25	100	120	140		
SPEEK (0.9)/SiPPSU (7%)	7.7	47.0	72.0	90.9	201	170
SPEEK (0.75)/SiPPSU (7%)	6.4	28.8	31.1	38.3	193	170

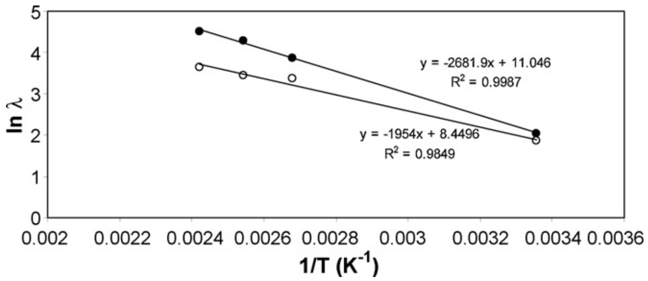

Fig. 6. Temperature dependence of the water uptake coefficients of blends: SPEEK 0.9–7% SiPPSU (●), SPEEK 0.75–7% SiPPSU (○).

SPEEK. In our case, the DS effect is largely reduced in the blends with SiPPSU.

In literature, tensile strength of sulfonated polymers decreases often with increasing degree of sulfonation [33]. However, these results can be explained by the presence of a larger quantity of water, which is correlated to the amount of sulfonate groups: the sorbed water molecules are acting as membrane plasticizer. A similar compensation effect might also be responsible for the nearly constant Tg value with various DS, as described before.

3.2. Water uptake coefficients

Fig. 5 shows water vapour adsorption/desorption isotherms of SPEEK 0.9 and blend at 25 °C. The water uptake coefficient of blend around RH = 60%, which is about ambient humidity, is consistent with the value calculated above from the initial water loss in TGA. The water vapour uptake of pure SPEEK is higher than for the blend, in agreement with the hydrophobicity of SiPPSU secondary phase.

Water uptake coefficients measured by immersion in liquid water between 25 and 140 °C are summarized in Table 1. No dissolution is observed, even at 140 °C, in contrast with pure SPEEK. Using water uptake coefficients λ at different temperatures, one can estimate the activation energy Ea from an Arrhenius plot using the equation:

$$\ln\ \lambda = \ln \lambda^{\circ} - \frac{Ea}{RT} \qquad (2)$$

Linear correlations are indeed observed (Fig. 6), confirming the applicability of Arrhenius equation; the calculated activation energies, around 20 kJ mol^{-1}, are in good agreement with activation energy values for water diffusion in SPEEK (17–20 kJ mol^{-1} [34]). Given that the membrane composition changes during water uptake, the temperature dependence is assumed to be related to chemical diffusion of water, including thus a term related to activity coefficients of water. The activation energy includes the partial molar enthalpy of water in the polymer matrix. The slightly lower activation energy value for the sample with smaller DS might be related to a smaller partial molar enthalpy of water in the less sulfonated polymer; this would correspond to a lower amount of hydrogen bonding between sulfonic acid groups and water.

3.3. Thermo-electrical properties

Fig. 7a presents the AC conductivity of a SPEEK 0.75 blend membrane measured under dry argon as function of measurement frequency and temperature, up to 200 °C; Fig. 7b shows a full

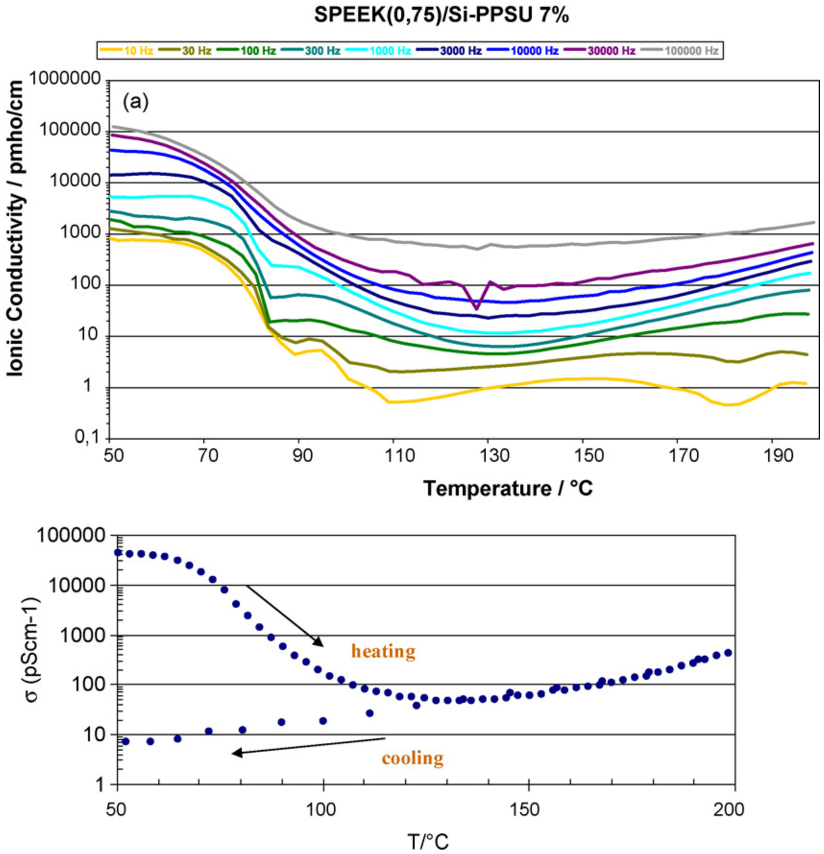

Fig. 7. AC conductivity of a SPEEK 0.75/SiPPSU blend membrane as function of temperature, (a) at all frequencies between 10 Hz and 100 kHz during heating (b) at 10 kHz during heating and cooling successively.

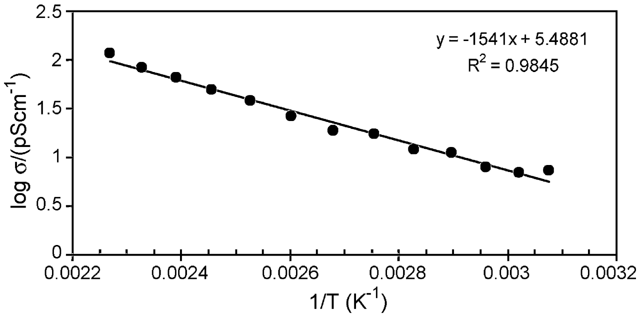

Fig. 8. Arrhenius plot of AC conductivity of anhydrous SPEEK 0.75/SiPPSU from DEA measurements.

heating/cooling cycle at fixed frequency 10 kHz. The corresponding experiments were impossible for pure SPEEK, because the membrane bonded to the electrode arrangement. The AC conductivity is deduced from dielectric loss data using Eq. (1). From Fig. 7, it is apparent that the temperature dependence of AC conductivity is quite similar at all observed frequencies. The very low conductivity observed corresponds to a polymer with low DS and much reduced water content. The AC conductivity drops further above 80 °C and reaches an intermediate minimum around 130 °C, due to the water loss, before a slight increase is observed, corresponding to the softening of the polymer chains, consecutive to glass transition. The polymer chain movements can support ion hopping above T_g. On cooling, the conductivity decreases monotonically: at room temperature, the fully anhydrous polymer behaves like an insulator, similar to analogue polymeric proton conductors [34,35]. The temperature dependence of AC conductivity on cooling below the glass transition temperature (Fig. 8) is in good agreement with Arrhenius equation, as expected, and the deduced apparent activation energy is about 30 kJ mol^{-1}, in excellent agreement with previous results on SPEEK/SiPPSU [8].

Fig. 9 shows the proton conductivity of SPEEK 0.9 blend at 100 °C, deduced from impedance spectroscopy, as function of relative humidity in a semi-logarithmic plot, in comparison with neat SPEEK (DS = 0.9) from Ref. [16]. Given the approximately exponential increase of the water uptake coefficient with relative humidity (Fig. 5), the linear dependence observed indicates an approximately linear increase of proton conductivity with water uptake coefficient, as previously reported for different proton conducting membranes [36]. The blend conductivity is nearly coincident with the conductivity of pure SPEEK up to about 80% RH. At RH values above 85%, SPEEK membranes become dimensionally unstable due to the large swelling and the conductivity decreases drastically. The conductivity of the blend turns out to be stable up to at least 90% RH; it is therefore fully compatible with fuel cell operation in this humidity domain. This is another important membrane improvement by composite formation with SiPPSU.

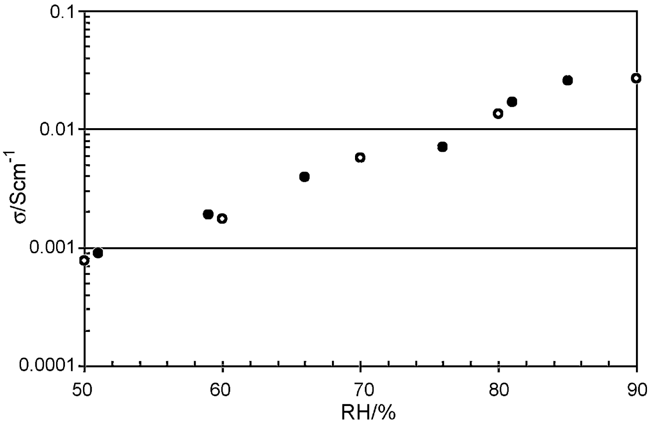

Fig. 9. Proton conductivity *vs.* relative humidity for SPEEK 0.9/SiPPSU (○) , SPEEK 0.9 (●) measured by EIS at 100 °C.

4. Conclusions

Polymer composites of highly sulfonated SPEEK and SiPPSU were studied in terms of mechanical, thermal and electrical properties and compared with pure SPEEK. Presence of silicon stabilizes the polymer morphology.

We observe superior behaviour of the composite, such as a much increased glass transition temperature, as shown by dynamic mechanical analysis. Water uptake coefficients are spectacularly lower than those of pure SPEEK, which is water soluble, even at 140 °C. Proton conductivity decreases above 85% RH for pure SPEEK, but continues to increase for the polymer blend.

Self-assembly of composite membranes is a promising approach for mechanically stable, high-performance PEMs for fuel cells.

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